Publication No. 02-03-088

Analysis of Fish from Long Lake, Washington, for PCBs and Selected Metals

Quality Assurance Project Plan

By
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February 12, 2002

Waterbody No. 54-9040
Long Lake - Lower Spokane River

Washington State Department of Ecology
Environmental Assessment Program
Olympia, WA 98504-7710

Approvals:

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Stuart Magoon, Manchester Laboratory Director — February 25, 2002 Date

Cliff Kirchmer, Ecology Quality Assurance Officer — Feb. 25, 2002 Date

Background and Problem Statement

In the Spokane River, upstream from river mile 58.1 at Nine-Mile Dam, elevated polychlorinated biphenyls (PCBs) have been historically detected in sediments and fish tissue (Johnson, 1997; Johnson, 2000). Concentrations in fish tissue from the Spokane River above Nile-Mile Dam have been high enough to warrant an ecological risk assessment (Johnson, 2001a) and the issuance of a human fish consumption advisory (Spokane County Health Department, 2001). The Upper Spokane River health advisory for fish is issued jointly by the Washington State Departments of Ecology (Ecology) and Health (DOH) and the Spokane Regional Health District.

Both lead and PCBs have been found in rainbow trout, mountain whitefish, and largescale suckers from the Upper Spokane River at concentrations that pose a risk to consumers. Metals concentrations, especially lead, cadmium, and zinc, are elevated in the Spokane River system due to contributions from the Coeur d'Alene Basin Mining Districts and nearby tributaries in Idaho (USEPA, 1988). Various PCBs are known to enter the river from industrial sites in Spokane (Golding, 2001). Of the three species with elevated lead and PCB concentrations in the Upper Spokane, mountain whitefish and largescale suckers also live in portions of Long Lake. To date, an insufficient number of tissues have been analyzed from downstream reaches of the Spokane River system to evaluate potential human or ecological risks from metals or PCBs below Nine-Mile dam.

Project Description

In July of 2001, the Washington Department of Fish and Wildlife (WDFW) conducted a comprehensive population survey of fish in Long Lake. Ecology's Eastern Regional Office coordinated the joint collection of fish by Environmental Assessment Program (EAP) biologists to evaluate fish tissue PCB and metals concentrations. Ecology and DOH will use these data to evaluate human fish consumption and ecological risks in Long Lake.

For the EAP collection efforts, two lake strata were established and EAP/WDFW personnel targeted the collection of 30 fish from 5 species from each zone. Because sediment PCB concentrations vary within Long Lake (Johnson, 2001b) and fish tissue concentrations may also vary, an upper and a lower lake strata were established. These two strata were defined using WDFW specified bank reaches (Figure 1). The 30 fish targets were established to provide 3 composite samples of 10 fish each. These numbers are necessary to establish, with high confidence, the mean contaminant concentration in the fish tissues. The human health risk assessment performed by DOH will be based upon these means.

The species list includes yellow perch, large and smallmouth bass, large-scale sucker, and mountain whitefish. Due to habitat requirements, mountain whitefish are only found in the upper lake. Rainbow trout are one of the species of concern in the upper river, and the joint Ecology/DOH Spokane Regional Health District health advisory addresses this species. However, rainbow trout are not found in the lower river. Brown trout were targeted as a surrogate species but only four brown trout were caught during the survey. Thus, a field decision

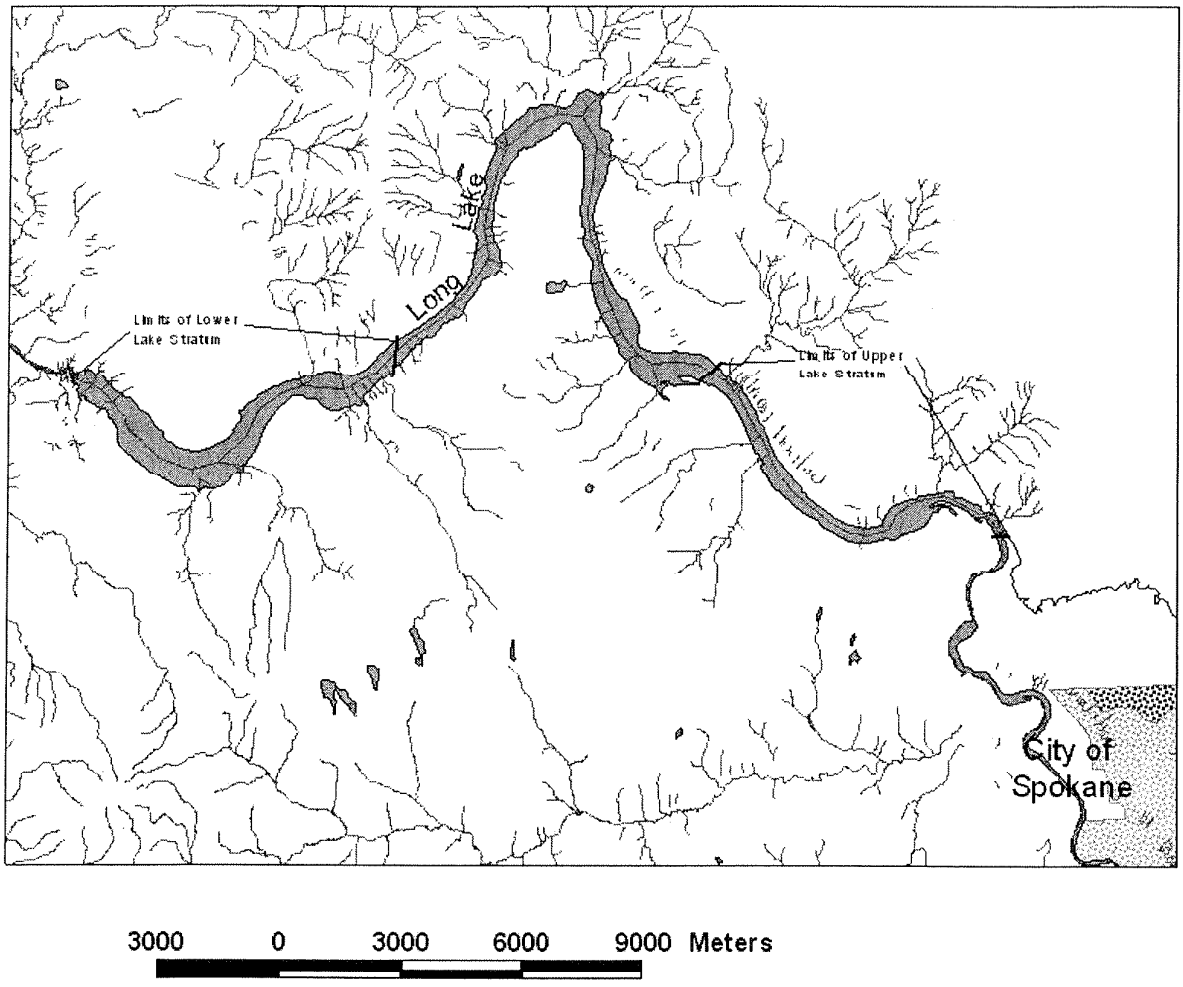

Figure 1. Long Lake, WA Fish Sampling Strata

was made to collect smallmouth bass instead. Based on discussions with WDFW biologists, the species list represents the commonly caught, edible fish tissue in Long Lake.

All fish were weighed, measured, double wrapped in aluminum foil, placed in plastic bags, and stored frozen at -18^0 C. This QAPP addresses the composite procedures and chemical analysis of these fish tissues. The chemical analysis includes PCB Aroclor equivalents, PCB congeners, lead, cadmium, zinc, and mercury. Organic analytes, lead, cadmium, and zinc will be used for human health risk assessment by the DOH. Ecology will evaluate these constituents relative to ecological standards and prior Upper Spokane investigations. Mercury will be analyzed to determine if future investigations should include this analyte.

Project Organization

Client – John Roland (509/625-5182)
Project Lead – Richard Jack (360/407-6139)
Sample Prep – Richard Jack and Morgan Roose (360/407-6458)
Toxic Studies Unit Supervisor – Dale Norton (360/407-6765)
Section Manager – Will Kendra (360/407-6698)
Quality Assurance Manager – Cliff Kirchmer (360/407-6455)
Manchester Laboratory Director – Stuart Magoon (360/871-8801)

Schedule

Laboratory Processing and Compositing – February 2002 (performed at Ecology Headquarters)
Chemical Analysis Complete – April 2002
Data Tables Provided to DOH – May 2002
Draft Ecology Report – June 2002
Final Ecology Report – August 2002

Measurement Quality Objectives

Accuracy, Bias, and Precision

In an effort to minimize bias, Puget Sound Estuary Program (PSEP) (USEPA, 1997) guidelines for collecting, preserving, transporting, and storing tissue samples will be followed. Acceptable accuracy shall be 25%. The bias goal will be 10% for metals and as defined as acceptable in the organic methods. These goals will principally be evaluated through the analysis of matrix spikes and laboratory control samples. The goal for precision will be 10 and 50% RSD for metals and organics respectively. The precision goals are subject to discretion depending upon the results relative to the detection limits. Table 1 summarizes the accuracy, bias, and precision goals for the project.

Table 1. Accuracy, Bias, and Precision Goals for Long Lake Fish Analysis, with Target Reporting Limits.

Parameter	Accuracy (% Deviation from True Value)	Bias	Precision (RSD)	Target Reporting Limit (µg/Kg, Wet)
Lead	30%	±10%	10%	10 – 100
Zinc	30%	±10%	10%	10 - 1000
Cadmium	30%	±10%	10%	10 – 100
Mercury	30%	±10%	10%	0.1 – 10
Aroclors	N/A	N/A[c]	50%	1 - 10
Selected PCB Congeners	Within reference windows[a]	N/A[b]	50%[b]	0.1 - 0.5
Percent Lipids	N/A	N/A	10%	0.1%

[a] Accuracy is based only upon those congeners for which certified values are available.
[b] Precision and bias for all PCB congeners based on isotope spikes as described in the methods.
[c] Because Aroclors are mixtures of congeners, and pattern identification is subject to weathering and analytical interpretation, total bias cannot be predicted. Data will be used qualitatively.

Experimental Design

Representativeness

The objective of the study is to describe the nature and extent of fish contaminant concentrations in Long Lake fish. Two lake strata have been established: Upper and Lower Long Lake. Lower Long Lake is defined as the reach of the Spokane River between Long Lake Dam and a line drawn between the following points at N 47°50'32.46", W 117°43'25.42" and N 47°50'0.67", W 117°43'56.51". Upper Long Lake is defined as the river/lake reach upstream of a line between N 47°49'43.91", W 117°37'46.21" and N 47°49'57.41", W 117°37'27.34". Upper Long Lake ends at a line drawn between N 47°47'37.23", W 117°32'6.71" and N 47°47'39.16", W 117°31'53.0". Figure 1 illustrates the lake strata.

Although 30 fish from each species were targeted, collection of sufficient fish was not possible for all species. Composite samples, which range in size from 4 to 10 fish per composite, have been collected using electroshocking and gill and fyke nets from each lake segment. The composite size goals were developed in consultation with Bill Griffith of the University of Washington. Dr. Griffith will collaborate with the DOH to develop representative metrics for human health risk assessment purposes. The fish collected represent the edible fish available in Upper and Lower Long Lake.

Comparability

Sampling methods were consistent with PSEP protocols (USEPA, 1997) and prior fish sampling in the upper Spokane River. Thus, results from this study should be comparable with previous studies on the upper Spokane River. Some composites are larger than used in previous studies. The larger composites, of up to 10 fish each, will allow for greater accuracy and precision in estimating the mean tissue concentrations of the population.

The metals and PCB Aroclor analytical methods selected for this study are consistent with prior analyses. Prior studies on the Spokane River have not always analyzed for PCB congeners. However, the proposed congener analytical methods are industry standards and the 150-congener list is consistent with prior EAP studies.

Sampling Methods

Fish were collected over two nights and one day using both electrofishing, and gill and fyke netting techniques. At the end of each sampling effort, fish were weighed and their length measured. Some fish weights and lengths were not recorded as their heads required removal to extract the fish from the gill and fyke nets.

Fish were then wrapped in aluminum foil, placed in polyethylene bags, and held on ice. All fish were assigned an identification number and letter code, the latter corresponds to their lake strata. Fish were then transported to the EAP storage facilities and frozen at -18^0 C.

Aging structures will be removed from all fish prior to tissue preparation. The following structures will be removed by EAP biologists and provided to WDFW for aging.

Table 2. Aging Structures to be Removed from Fish by Species

Species	Aging Structures Removed
Largemouth Bass	Scales, otoliths, opercles, dorsal spines
Largescale Sucker	Scales, opercles
Mountain Whitefish	Scales, otoliths
Smallmouth Bass	Scales, otoliths, opercles, dorsal spines
Yellow Perch	Scales, otoliths, opercles, dorsal spines

Exact fish collection locations were not identified in the field. To facilitate tissue data entry into Ecology databases, the approximate midpoint of the lake strata will be determined using maps or Arcview. All fish collected within a stratum will be assigned this location point.

Tissue Preparation

Preparation of tissue samples will follow USEPA (1997 and 2000) guidance. The techniques described below will be used to minimize the potential for sample contamination and cross-contamination.

All resection and homogenizing will use only non-corrosive stainless steel implements. Persons preparing samples will wear non talc polyethylene or nitrile gloves and work on aluminum foil or a polyethylene cutting board. Gloves and foil will be changed between composite samples. The cutting board and knives will be cleaned using Liquinox® detergent and hot tap water,

followed by rinses with 10% nitric acid, deionized water, and pesticide grade methanol. Implements will be air dried in a fume hood before use.

Fish will be thawed only enough to remove their aluminum foil wrapping and aging structures. Fish will then be rinsed with tap water followed by deionized water. For fillets, the fish will be descaled but skins will be left on. The entire fillet tissue will be removed and homogenized before weighing out an aliquot for compositing. Fillets will minimize the inclusion of scales or bones, which could bias metals results.

Homogenized tissues will be placed in glass or polyethylene jars with Teflon lids; precleaned to USEPA (1990a) QA/QC specifications. All composite samples, by species, will contain equal numbers of fish. Each composite sample will contain 100 grams of tissue, comprised of an equal mass of each individual fillet. For each species, the individual fish will be pooled as shown on Table 3.

Table 3. Fillet Composite Sizes for Upper and Lower Long Lake Fish Fillets by Species.

Upper Lake Species	Composite Size	Lower Lake Species	Composite Size
Largemouth Bass	10 fish	Largemouth Bass	4 fish
Largescale Sucker	10 fish	Largescale Sucker	9 fish
Mountain Whitefish	6 fish	Smallmouth Bass	6 fish
Smallmouth Bass	5 fish	Yellow Perch	11 fish
Yellow Perch	10 fish		

Three whole suckers will also be selected from both the Upper and Lower Lake strata. These six suckers will be analyzed for lead, zinc, cadmium, and PCB Aroclors. Whole fish will be homogenized in a Hobart commercial meat grinder and include all scales, bones, slime, and associated liquids. Meat grinders will be cleaned between samples with Liquinox®, nitric acid, and methanol using the same procedures described above for cutting boards and knives.

Each sample will be divided into sample jars to facilitate laboratory handling and extraction. The mass per each container will be as shown on Table 4.

Table 4. Sample Sizes and Containers by Parameter for Long Lake Fish Tissues

Parameter	Sample Size	Container	Number Composite Samples	Number Whole Fish Samples	Holding Time (Frozen)
Metals (Pb, Zn, Cd)	20 g	Glass w/ Teflon lined lid	24	2	2 years
Mercury	20 g	Glass w/ Teflon lined lid	6	0	28 days
PCB Aroclors	30 g	Glass w/ Teflon lined lid	43	6	1 year
PCB Congeners	30 g	Glass w/ Teflon lined lid	20	0	1 year

Analytical Methods

Metals, PCB Aroclors, and lipid samples will be analyzed at Manchester Laboratory. The 150 PCB congeners will be analyzed at a commercial laboratory. Analytical methods are suggested in Table 5. Other methods may be used at the discretion of Manchester or the contract laboratory after consulting with the project lead.

Table 5. Preparation Methods, Analytical Methods, and Necessary Reporting Limits

Analyte	Preparation Method	Analytical Method	Expected Maximum Tissue Reporting Limit (µg/Kg, Wet)
Lead	Microwave digestion, EPA Method 3051A (USEPA, 1994a)	ICP/MS, EPA Method 200.8 (USEPA, 1994b)	100
Zinc	Microwave digestion, EPA Method 3051A (USEPA, 1994a)	ICP/MS, EPA Method 200.8 (USEPA, 1994b)	1000
Cadmium	Microwave digestion, EPA Method 3051A (USEPA, 1994a)	ICP/MS, EPA Method 200.8 (USEPA, 1994b)	100
Mercury	Aqua regia + oxidizing permanganate (MEL 2001)	CVAA, EPA Method 245.6 (USEPA, 1991)	5
Aroclors	Soxhlet extraction (USEPA, 1996)	GC/ECD, EPA Method 8082 (USEPA, 2000)	1 -10
PCB Congeners	Soxhlet extraction (USEPA, 1996)	GC/ECD, EPA Method 1668A (USEPA, 1999)	0.001 – 0.050
Percent Lipids	N/A	Gravimetric (USEPA, 1990b)	0.1%

Not all species or samples will be analyzed for every constituent. Table 6 describes the number of analyses planned by species for the Upper Lake, while Table 7 describes the numbers and types of fish tissue samples to be analyzed by species for the Lower Lake. Both tables also illustrate the number of composite splits and matrix spikes analyzed. Congener analysis is planned for large-scale suckers and for largemouth bass. These species were selected for individual congener identification because: 1) they reach larger sizes and are thus more valued by fishermen, 2) they represent two guilds, pelagic predators and bottom feeding detritivores, which are believed to have the greatest PCB bioaccumulation and exposure respectively.

Table 6. Number of Upper Lake Fish Tissue Samples by Analysis Type by Species*.

Species	Aroclors	Congeners	% Lipids	Metals (Pb, Zn, Cd)	Mercury
Yellow Perch	3		3	1	
Largemouth Bass	3	3	3	3	3
Largescale Sucker (Whole)	3		3	1	
Largescale Sucker	3	3	3	3	
Smallmouth Bass	3		3	1	
Mountain Whitefish	3	3	3	1	
Composite Split	3	1	2	1	
Matrix Spike	2	2		2	
Total	**23**	**12**	**18**	**13**	**3**

*All rows are composite samples except where noted.

Table 7. Number of Lower Lake Fish Tissue Samples by Analysis Type by Species*.

Species	Aroclors	Congeners	% Lipids	Metals (Pb, Zn, Cd)	Mercury
Yellow Perch	3		3	1	
Largemouth Bass	3	3	3	3	3
Largescale Sucker (Whole)	3		3	1	
Largescale Sucker	3	3	3	3	
Smallmouth Bass	3		3	1	
Composite Split	3	1	1	1	
Matrix Spike	2	1		1	
Total	**20**	**8**	**16**	**11**	**3**

*All rows are composite samples except where noted.

Because fish were collected last summer in cooperation with WDFW, sample holding times for mercury have already been exceeded. The mercury analysis will not be used for risk assessment purposes and future data reporting will note the discrepancy. Table 8 provides the estimated analytical costs for the analyses by sample.

Table 8. Sample Numbers and Analytical Costs for Long Lake Fish Tissue Samples

Sample Type	Analysis	Tissues	Split Samples	Spike Samples	Total	Unit Cost	Subtotal Cost
Upper Lake	Aroclors	18	3	2	22	$150	$3,300
	Congeners	9	1	2	12	$1,200	$14,400
	% Lipids	18	2		20	$31	$620
	Metals (Pb, Zn, Cd	10	1	2	13	$136	$1,768
	Mercury	3			3	$50	$150
Lower Lake	Aroclors	15	3	2	18	$150	$2,700
	Congeners	6	1	1	8	$1,200	$9,600
	% Lipids	15	1		16	$31	$496
	Metals (Pb, Zn, Cd	9	1	1	11	$136	$1496
	Mercury	3			3	$50	$150
Certified Reference Material	National Institute of Standards and Technology, SRM 2977 (frozen mussel tissue)				1	$361	$361
	Congeners	1			1	$1,200	$1,200
	National Research Council of Canada (NRC), DOLT-2 (frozen dogfish muscle)				1	$150	$150
	Metals: Cd, Pb, Zn, Hg	1			1	$186	$186
						Total Cost	**$37,027**

Quality Control Procedures

Field/Processing Measures

To estimate sampling precision, two splits will be performed on the Upper Lake Aroclor composites, while one split will be performed on the Lower Lake Aroclor samples. For congener and metals analysis, one split will be performed on both Upper and Lower Lake composites. The splits will not be identified to the laboratory.

Laboratory Measures

The QC procedures routine to the methods cited in Table 4 will be satisfactory for this project. As shown on table 7, selected samples will receive matrix spikes to estimate analytical bias due to matrix interference or other affects. For organics, acceptable spike bias varies by analyte and is defined in the methods. For metals, acceptable spike bias is 25% RSD.

Precision will be estimated in the laboratory using control samples and analytical duplicates. These will be conducted at a frequency of one per sample batch. Lab matrix spike duplicates should be ±25% and laboratory duplicates ±20%. Table 9 documents the necessary laboratory QC procedures.

Reference Materials

Frozen mussel (*Mytilus edulis*) certified reference materials will be analyzed for PCB Congeners. This certified reference tissue (SRM 2977) will be obtained from the National Institute of Standards and Technology in Gaitherburg, MD. This tissue is not certified for all the metals of interest in this study. Therefore, frozen dogfish muscle (*Squalus acanthias*) (DORM-2) certified reference materials will be obtained from the National Research Council of Canada (NRC) and analyzed for the four metals of interest. Acceptable reference material organics accuracy is within the windows provided by the reference material supplier. Reference material metals accuracy shall be within 20%. This objective is within the reference material window(s) as specified by the suppliers.

Table 9. Laboratory Quality Control Measures and Frequency by Parameter.

Parameter	Check Standards	Method Blanks	Analytical Duplicates	Matrix Spike & Duplicate	Reference Materials
Lead	10%	1 per batch	1 per batch	1 per batch	1 per batch
Zinc	10%	1 per batch	1 per batch	1 per batch	1 per batch
Cadmium	10%	1 per batch	1 per batch	1 per batch	1 per batch
Mercury	10%	1 per batch	1 per batch	1 per batch	1 per batch
Aroclors	10%	1 per batch	1 per batch	1 per batch	None
PCB Congeners	10%	1 per batch	1 per batch	1 per batch	1 per batch
Percent Lipids	None	None	1 per batch	None	None

Data Review, Verification, Validation, and Reporting

The project manager will review all data and analytical narratives for completeness, bias, and precision goals. The data will be verified against the data quality objectives stated above and then tabulated, their quality summarized, and these tables will be provided to DOH. The Department of Health will be responsible for any additional DQOs necessary for completion of the risk assessment.

Data Quality Assessment

A draft data report will be prepared by EAP. The Washington State Department of Health will receive a copy of the draft report for their use. Completion of the draft report is anticipated by May 2002. The report will include:

1) A map of the study area showing lake strata
2) Descriptions of field and laboratory methods
3) Sample information including lengths, weights, and ages (if available from the WDFW in a timely manner) of fish sampled and composited
4) Discussion of data quality and any significant analytical problems
5) Summary tables of analytical data
6) Comparisons of data with previous work on the Upper Spokane and ecological risk standards
7) Recommendations for follow-up work as warranted
8) An appendix of analytical case narratives

Comparisons with previous analytical results from the Upper Spokane River will consider the estimates of accuracy, precision, and bias available.

Project data will be entered in Environmental Information Management (EIM) prior to completion of the final report.

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